PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 3, 03TF12(3pp) (2012)

Raman and Photoluminescence Study of ZnO Films Grown by Chemical Method

K.A. Avramenko*, A.S. Romanyuk, V.V. Strelchuk, O.F. Kolomys, L.V. Zavyalova, S.V. Svechnikov, B.A. Snopok, N.N. Roshina

V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, prospect Nauky, 03028 Kyiv, Ukraine

(Received 17 June 2012; published online 22 August 2012)

In this paper phonon and emission properties of ZnO films grown by metalorganic chemical vapour deposition (MOCVD) at ambient pressure and by molecular beam epitaxy (MBE) are investigated using Raman and photoluminescence (PL) spectroscopy. It is shown that high-frequency shift of non-polar phonon modes corresponds to elastic compressive strain in the plane parallel to c-axis and is equal to 3.2×10^{-3} and 2.2×10^{-3} for ZnO film grown by MOCVD and MBE, respectively. The possibility of obtaining high-quality ZnO films grown by MOCVD was demonstrated.

Keywords: ZnO film, Raman spectroscopy, Photoluminescence, strain, MBE.

PACS numbers: 33.20.Fb, 78.55.Et

1. INTRODUCTION

ZnO films are actively studied due to their unique properties for practical applications in the UV detectors, field emission displays, thin film transistors, solar cells, biosensors and etc.

Up to now, most ZnO films have been prepared by various methods such as magnetron sputtering, impulse laser deposition and MBE. The most perfect crystal structure of ZnO films are obtained by MBE. However, MBE method is quite expensive. Therefore, the development of alternative, more simple and less costly growth method that allows obtaining high-quality ZnO films is an actual problem.

In this paper Raman and PL spectroscopy were used to determine the structural and emission properties of ZnO film grown by modified MOCVD. The properties of this film have been compared with the properties of ZnO film obtained by MBE. Frequency position analysis of nonpolar E_2^{high} phonon mode allowed estimating the elastic strain and the crystal quality of ZnO films.

2. EXPERIMENT

Two types of ZnO films were investigated: first one was grown by MOCVD at ambient pressure on glass substrate (spraying an organic solution of organometallic compounds and heated to 300C glass substrate similar to [1]); second film was grown by MBE on c-plane sapphire (Al_2O_3) substrate [2].

Micro-Raman and PL spectra were excited using lines of Ar^+/Kr^+ ion laser (488.0 nm) and He-Cd laser (325.00 nm), respectively. Spectra were collected by Jobin-Yvon T64000 triple spectrometer equipped with a CCD detector and Olympus BX41 microscope with ×100 objective (NA = 0.90). Spectral resolution was about 0.15 cm^{-1}.

3. RESULTS AND DISCUSSION

Figure 1 shows the micro-Raman spectra of ZnO films grown by MOCVD and MBE. Phonon modes corresponding to E_2^{low}, E_2^{high}, $E_2^{high} - E_2^{low}$ and A_1^{LO} of ZnO wurtzite crystal structure are present in the Raman spectra of ZnO films. Weak peaks at 332.0 and 576.0–580.0 cm^{-1} correspond to $E_2^{high} - E_2^{low}$ difference two-phonon and A_1^{LO} polar modes of ZnO films, respectively.

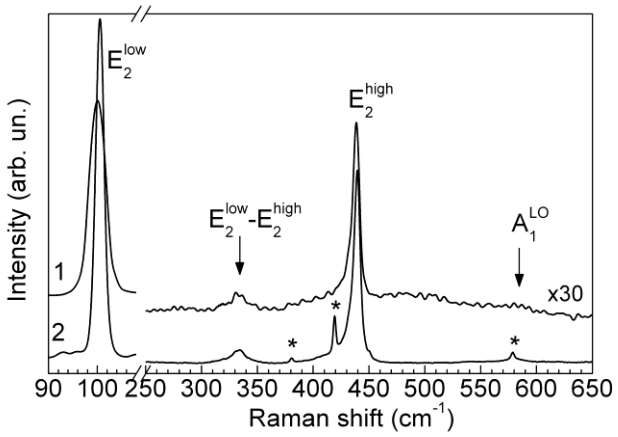

Fig. 1 – Micro-Raman spectra of ZnO films grown by MOCVD (curve 1) and MBE (curve 2). Asterisk indicates the sapphire substrate phonon modes at 379.6, 419.2 and 578.4 cm^{-1}. λ_{exc} = 488.0 nm, T = 300 K

Non-polar E_2^{low} mode is observed at ≈ 100.1 and 100.6 cm^{-1} for ZnO films grown by MOCVD and MBE, respectively (Fig. 2a). Low frequency shift of E_2^{low} mode as compared to the frequency for bulk ZnO (ω_0 = 101.0 cm^{-1}) is caused by biaxial compressive strain in the plane perpendicular to the c-axis. The fact that the halfwidth of nonpolar E_2^{low} mode of ZnO film grown by MOCVD (≈ 3.8 cm^{-1}) is higher than the halfwidth for ZnO film grown by MBE (≈ 1.7 cm^{-1}) indicates higher structural quality in zinc sublattices of the latter film [3].

* yessss@yandex.ru

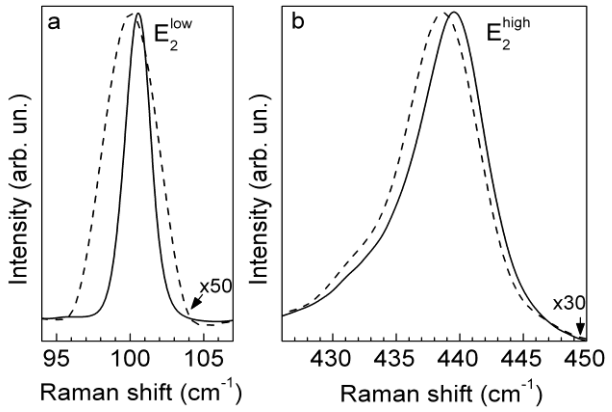

Fig. 2 – Micro-Raman spectra of ZnO films grown by MOCVD (dash curve) and MBE (solid curve) in the frequency range o E_2^{low} (a) and E_2^{high} (b) phonon modes. λexc = 488.0 nm. T = 300 K.

The value of biaxial strain ε_{zz} along the c-axis of ZnO films is determined by the frequency shift $\Delta\omega(E_2^{high})$ [4]:

$$\varepsilon_{zz}^{(\Delta\omega)} = (\omega - \omega_0) / (b - a(C_{33}/C_{13})) = \Delta\omega(E_2^{high}) \cdot \mathrm{K}\,.$$

For strain-free ZnO: $\omega_0 = 437.0$ cm^{-1} – frequency of E_2^{high} phonon mode; $a = -690$ cm^{-1} and $b = -940$ cm^{-1} – phonon deformation potentials; $C_{13} = 90$ GPa and $C_{33} = 196$ GPa – elastic constants. The observed high – frequency shift of the E_2^{high} mode by $\Delta\omega_{E_2} = \omega - \omega_0 \approx 1.7$ and 1.2 cm^{-1} corresponds to the biaxial compressive strains $\varepsilon_{zz} \approx 3.2\times10^{-3}$ and 2.2×10^{-3} for ZnO films grown by MOCVD and MBE, respectively (Fig. 2b). Using Poisson ratio ($\varepsilon_{xx}^{(\Delta\omega)} = -\varepsilon_{zz}^{(\Delta\omega)} C_{33} / 2C_{13}$), the value of ε_{xx} strain perpendicular to c-axis is equal to $\approx -3.5\times10^{-3}$ and -2.4×10^{-3} for ZnO films grown by MOCVD and MBE, respectively. The halfwidth of E_2^{high} phonon modes is equal to ≈ 6.9 and 6.0 cm^{-1} for ZnO films grown by MOCVD and MBE, respectively. This fact indicates high structural quality in oxygen sublattice for investigated ZnO films (Fig. 2b).

Multi-phonon *LO*-modes (up to 3*LO*) on the background of photoluminescence were observed in resonance Raman scattering of ZnO films. These *LO* modes correspond to an inelastic scattering on A_1^{LO} phonons of ZnO films (Fig. 3). In resonant Raman spectra, the increase of *LO* phonons intensity as well as the high order one phonon A_1^{LO} modes is caused by the Froehlich electron-phonon interaction. The difference of A_1^{LO} phonon modes frequency for ZnO films grown by MOCVD (572.8 cm^{-1}) and MBE (575.9 cm^{-1}) as compared to the frequency for bulk ZnO ($\omega_0 = 574.0$ cm^{-1}) might be caused not only by elastic compression strain [5] but also by high concentration of free charge carriers in ZnO films [6]. The intensity ratio of second and first order *LO* phonon modes I_{2LO}/I_{1LO} is equal to ≈ 1.9 and 1.2 for ZnO films grown by MOCVD and MBE, respectively. The obtained values I_{2LO}/I_{1LO} indicates the high efficiency of electron-*LO*-phonon interaction for investigated ZnO films [7].

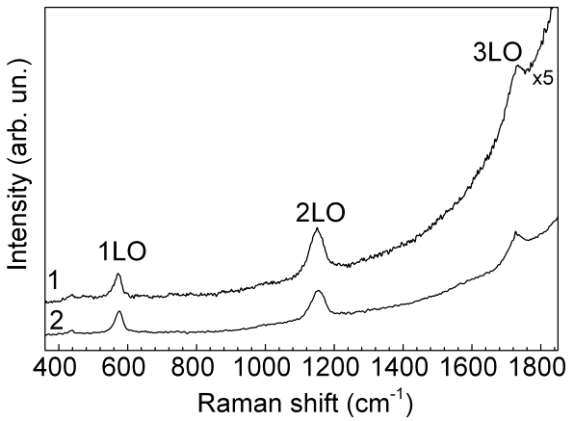

Fig. 3 – Resonant micro-Raman spectra of ZnO film grown by MOCVD (curve 1) and MBE (curve 2). $\lambda_{exc} = 488.0$ nm. $T = 300$ K.

The ultraviolet (UV) emission band with a maximum at ≈ 3.30 eV and the halfwidth at ≈ 60 eV was registered in PL spectra of ZnO films (fig. 4). This radiation is due to radiative recombination of localized excitons bound to neutral donors and/or acceptor [8]. The higher PL intensity of ZnO film grown by MBE (11 times) as compared to the intensity for ZnO film grown by MOCVD is caused by less amount of nonradiative recombination centers. Low-energy asymmetry of UV PL peak in ZnO films is modeled by two Gaussian contours. The fact that the distance between the maxima of these lines is equal to *LO*-phonon energy of ZnO indicates the high efficiency of radiative recombination with participation of *LO* phonons.

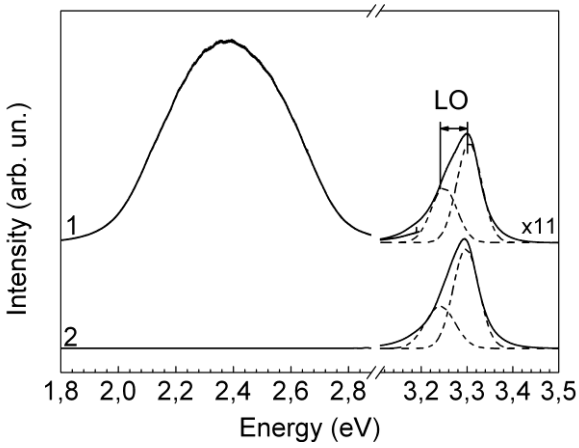

Fig. 4 – PL spectra of ZnO films grown by MOCVD (curve 1) and MPE (curve 2). Dash line – modeling by Gaussian contours. $\lambda_{exc} = 325.0$ nm. $T = 300$ K.

The intensive wide PL peak emission at 2.0–2.3 eV in ZnO film grown by MOCVD is also registered. It is associated with intrinsic point defects such as vacancies of oxygen (V_O), interstitial atoms of zinc (Zn_i) or oxygen (O_i) [9].

4. CONCLUSIONS

The phonon and emission properties of ZnO films grown by MOCVD and MBE were investigated by Raman and photoluminescence spectroscopy. The value of

elastic compressive strains and the crystal structure quality in zinc and oxygen sublattices of wurtzite ZnO films were characterized. The possibility of obtaining high-quality ZnO films suitable for optoelectronic devices by MOCVD technique at ambient pressure was demonstrated.

REFERENCES

1. G.S. Svechnikov, L.V. Zavyalova, N.N Roshchina, I.V. Prokopenko, L.I. Berezhinsky, V.S. Khomchenko, O.S. Lytvyn, *Semiconductor Physics, Quantum Electronics and Optoelectronics* **7**, 157 (2004).
2. J.P. Atanas, R.A. Asmara, A. Khoury, A. Foucaran, *Sensors and Actuators A* **127**, 49 (2006).
3. H. Harima, *J. Phys.: Condens. Matter* **14**, R967 (2002).
4. Th. Gruber, G.M. Prinz, C. Kirchner, R. Kling, F. Reuss, W. Limmer, A. Waag, *J. Appl. Phys.* **96**, 289 (2004).
5. X. Zhu, H. Wu, Z. Yuan, J. Kong, W. Shen, *J. Raman Spectrosc.* **40**, 2155 (2009).
6. J.D. Ye, S. Tripathy, Fang-Fang Ren, X.W. Sun, G.Q. Lo, K.L. Teo, *Appl. Phys. Lett*. **94**, 011913 (2009).
7. R.H. Callender, S.S. Sussman, M. Selders, R.K. Chang, *Phys. Rev. B.* **7**, 3788 (1973).
8. K. Thonke, T.H. Gruber, N. Teofilov, R. Schonfelder, A. Waag, R. Sauer, *Physica B* **308**, 945 (2001).
9. F.H. Leiter, H.R. Alves, A. Hofstaetter, D.M. Hofmann, B.K. Meyer, *phys. status solidi b* **226**, R4 (2001).